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# Selenium volatilization in vegetated agricultural drainage sediment from the San Luis Drain, Central California

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**Abstract**

The presence of large amounts of Se-laden agricultural drainage sediment in the San Luis Drain, Central California, poses a serious toxic threat to wildlife in the surrounding environment. Effective management of the drainage sediment becomes a practical challenge because the sediment is polluted with high levels of Se, B, and salts. This two-year field study was conducted to identify the best plant species that are salt and B tolerant and that have a superior ability of volatilizing Se from drainage sediment. The drainage sediment was mixed with clean soil, and vegetated with salado alfalfa (*Medicago sativa* 'salado'), salado grass (*Sporobulus airoides* 'salado'), saltgrass-turf (*Distichlis* spp. 'NYPA Turf'), saltgrass-forage (*Distichlis spicata* (L.) *Greene*), cordgrass (*Spartina patens* 'Flageo'), Leucaenia (*Leucaena leucocephola*), elephant grass (*Pennistum purpureum*), or wild type-*Brassica* (*Brassica* spp.). Results show that elephant grass produced the greatest amount of biomass and accumulated highest concentrations of B. Highest concentrations of Se, S, and Cl were observed in wild-type *Brassica*. Biogenic volatilization of Se by plants and soil microbes was greater in summer. Among the treatments, the mean daily rates of Se volatilization (μg Se $m^{-2}\,d^{-1}$) were wild-type *Brassica* (39) > saltgrass-turf (31) > cordgrass (27) > saltgrass forage (24) > elephant grass (22) > salado grass (21) > leucaenia (19) > salado alfalfa (14) > irrigated bare soil (11) > non-irrigated bare soil (6). Overall, rates of Se volatilization in drainage sediment were relatively low due to high levels of sulfate. To manage Se in drainage sediment by phytoremediation, the biological volatilization process needs to be enhanced substantially under field conditions.


*Keywords:* Drainage sediment; Selenium; Volatilization; Phytoremediation

## 1. Introduction

California's San Joaquin Valley (SJV) is one of the most productive irrigated agricultural areas in the world. Soils on the valley's western side were derived from cretaceous shale rocks and therefore contain high levels of natural-occurring selenium (Se) oxyanions, sulfate, and boron (B) salts. Inorganic forms of Se (e.g., selenate and selenite) are water soluble and mobile in soils, and dissolved in subsurface-tiled drainage water. Hence, transporting the agricultural drainage water in the 45-km long concrete-lined San Luis Drain resulted in the

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accumulation of over 100 000 $m^3$ of Se-laden drainage sediment (Quinn et al., 1998). Because of the presence of large amounts of Se, B and salts in the sediment, the need to dredge and remove the sediments from the San Luis Drain prompted research into practical means of their management and/or disposal.

Zawislanski et al. (2003) proposed land disposal of drainage sediment as an option due to its low cost, the proximity of large areas of available land to the drainage canal, and relatively low Se solubility in chemically reduced sediments (Tokunaga et al., 1996; Martens and Suarez, 1998). Because of the fact that concentrations of total Se have been reported to be as high as 186 mg $kg^{-1}$ in the drainage sediment (Zawislanski et al., 2001), and that excessive levels of Se accumulates in food chains, where it has caused death and deformation in waterfowl (Ohlendorf et al., 1986), it is imperative that new strategies be employed to manage the Se-polluted drainage sediment in the San Luis Drain. These may include the use of phytotechnology to stabilize Se at the polluted site (Bañuelos, 2002) and remove Se from the drainage sediment to the atmosphere via biological volatilization (Frankenberger and Karlson, 1989a,b; Lin and Terry, 2003).

For the management of Se in contaminated soil, Bañuelos (2002) has successfully field tested *Brassica* species (e.g., canola and broccoli) that are able to accumulate Se under saline conditions, and help reduce soluble Se levels in the soils. If a plant-based technology is to be considered as a part of any long-term Se remediation strategy for the drainage sediment in the San Luis Drain, the plants must be salt and B tolerant because high levels of sulfate, salt, and B in the sediment can reduce biomass yields (Wu et al., 1997; Maas and Grattan, 1999). When phytotechnology is applied for the remediation of Se-laden sediment, different plant species must be examined for their phytoextraction and volatilization capacities due to high levels of sulfate accumulated in the drainage sediment. Sediment sulfate reduces a plant's ability to phytoextract and volatilize Se from the sediment (Zayed and Terry, 1994). Moreover, sustainable use of plants for the remediation of Se in drainage sediment will be dependent upon the low maintenance efforts associated with growing plants or the compatibility of using selected annual plants in rotation with others on the disposal site.

Volatilization of Se by plants and microbes is an environmentally important approach in which Se can be dissipated from Se-laden sediments (Frankenberger and Karlson, 1994; Lin et al., 2000; Lin and Terry, 2003). Volatile Se compounds (e.g., dimethyl selenide and dimethyl diselenide) are formed through biomethylation, a biological process in which microorganisms and/or plants convert inorganic Se into methylated Se (Lewis et al., 1974; Zieve and Peterson, 1984; Terry and Zayed, 1998). The resultant methylated forms of Se are subject to volatile losses into the atmosphere from soils and waters. From an environmental perspective, biological volatilization may be a favorable pathway of Se removal because dimethyl selenide is reportedly ~500 times less toxic than the inorganic forms of Se (McConnell and Portman, 1952; Wilber, 1980), and because volatilization lowers the amount of Se available for entry into the food chain (Losi and Frankenberger, 1997; Zayed et al., 2000). Additionally, volatile Se produced from the San Luis Drain located in the western part of the San Joaquin Valley is most likely transported in the atmosphere out of the Valley to the surrounding mountainous regions and to other areas where soil Se is normally deficient (Lin et al., 2000).

Few field studies, to the best of our knowledge, have been made to measure Se volatilization under naturally occurring conditions. The measurements of Se volatilization were generally made by collecting volatile Se with transparent collection chambers, a procedure used in various forms by Biggar and Jayaweera (1993), Frankenberger and Karlson (1994), Lin et al. (1999, 2000), and Lin and Terry (2003). Earlier studies show that biological volatilization of Se varies greatly because of fluctuations in different physical, chemical, and biological factors in the field (Frankenberger and Karlson, 1989a,b, 1994; Allen, 1991; Jayaweera and Biggar, 1992; Rael et al., 1996; Hansen et al., 1998). Higher rates of Se volatilization were often observed when temperature, soil water content, and available organic carbon in soil were high (Frankenberger and Karlson, 1994; Gao and Tanji, 1995; Lin et al., 2000; Terry et al., 2000). However, because of high levels of B, sulfate, and salinity in the drainage sediment, the extent to which Se can be removed via biological volatilization from agricultural drainage sediment (the sediment with high levels of Se, B, and salts) has not been fully explored.

Thus, the objectives of this two-year study were to identify the best plant species that are salt and B tolerant and that have a superior ability of volatilizing Se from drainage sediment under field conditions, and to quantify the role of vegetation (vs. non-vegetation) in Se volatilization from drainage sediment.

## 2. Methods and materials

### 2.1. Field test plots

Drainage sediment was collected at 0–25 cm depth from the San Luis Drain, Mendota, CA, and spread to a depth of 40 cm in a previously excavated field plot in 2000 at the USDA Research Facility in Parlier, CA. Four centimeters of good quality soil (sandy loam; pH of 7.2, EC of 0.9 dS $m^{-1}$, and total Se concentration <0.1 mg $kg^{-1}$) was applied as cover soil and incorporated in a depth of 25 cm to essentially enhance plant survival (Bañuelos and Lin, 2005). Twenty beds were constructed on the field sediment plot, and each was 33-m long and 1-m wide. A surface drip irrigation system was installed consisting of one in-line turbulent flow emitter per bed with a 4 l $h^{-1}$ emitter discharge rate and emitter spacing of 0.45 m. Prior to planting, soil/sediment samples were collected every 10 m from the middle of each bed in 45-cm increments to a depth of 90 cm. Results from 0 to 45 cm depth of sediment were shown here in relation to this volatilization study.

### 2.2. Vegetation and field management

Vegetated plots consisted of planting perennial and one annual species that were selected because of their salt tolerance and hardiness (see Table 1). Each plant species was replicated on at least four 15 m × 1 m drainage sediment plots. Non-vegetated plots (i.e., bare soil) were also included with irrigation or without irrigation, as additional two treatments. Vegetation was started in the test plot by sowing and transplanting on April 1, 2002. The active growing seasons were defined from April 15 through December 15, 2002 and 2003 for the perennial plants and from May 1, 2002 through

Table 1
Plant species that were vegetated on the drainage sediment plots, including seven perennial and one annual species

| Species | Transplant | Source |
|---|---|---|
| Salado alfalfa (*Medicago sativa* 'salado') | Initially germinated from seed under greenhouse conditions, and planted 25-cm apart in double rows respectively as eight-week old clumps | Donated by Dr. Don Miller, ABI alfalfa, Nampa, Idaho |
| Salado grass (*Sporobulus airoides* 'salado') | Initially germinated from seed under greenhouse conditions, and planted 25-cm apart in double rows respectively as eight-week old clumps | Donated by Southwest Seed Inc. Doloros, CO |
| Saltgrass-turf (*Distichlis* spp. 'NYPA Turf') | Saltgrass-turf cuttings were initially irrigated with saline water (2–3 dS $m^{-1}$) under greenhouse conditions for eight weeks, and planted 25-cm apart in double rows | Donated by Dr. N. Yensen, Central Arizona College, Tucson, AZ |
| Saltgrass-forage (*Distichlis spicata* (L.) *Greene*) | Saltgrass-forage cuttings were initially irrigated with saline water (2–3 dS $m^{-1}$) under greenhouse conditions for eight weeks, and planted 25-cm apart in double rows | Donated by Dr. N. Yensen, Central Arizona College, Tucson, AZ |
| Cordgrass (*Spartina patens* 'Flageo') | Cordgrass plantlets were sustained under greenhouse conditions for eight weeks, clipped, and individually planted 25-cm apart in double rows | Donated by Dave Dyer, Plant Introduction Station, Lockeford, CA |
| Leucaenia (*Leucaenia leucocephola*) | Leucania cuttings were sustained under greenhouse conditions for eight weeks, clipped and individually planted 25-cm apart in double rows | Donated by Mort Rothberg, Fresno, CA |
| Elephant grass (*Pennistum purpureum*) | Stolons were removed from established field plants and planted 1-m apart in single rows | Donated by Mort Rothberg, Fresno, CA |
| Wild type-Mustard (*Brassica* spp.) | *Brassica* was germinated from seed and sustained under greenhouse conditions for six weeks and transplanted 25-cm apart in double rows | Collected along the North Coast, CA |

February 15, 2003 for wild-type *Brassica*. The perennial plants were dormant from December through March. Normal agronomic management practices were applied on the test plots, which included pre-plant application of fertilizer (16–6–16 without sulfur) at 50 kg $ha^{-1}$ each growing season, insect and animal (gopher) control, manual removal of weeds, and interval clipping (generally every 60 d) for all perennial plant species throughout the growing season. All perennial crops were clipped at least four times during each growing season of 2002 and 2003, whereas the annual crop, wild-type *Brassica*, was harvested after a 10-month growing season. During plant dormancy, all plots were left undisturbed under natural field conditions.

Vegetated and bare irrigated plots were drip irrigated based in part on both evapotranspiration losses recorded for bare plots and for each respective plant species located in duplicate on adjacent 15 × 1 m non-drainage sediment plots (sandy loam soil) and on weather data collected from California Irrigation Management Information System (CIMIS) weather station, located at University of California Kearney, Parlier, CA (approximately 2 km from the field site). The local meteorological conditions during the time of study are shown in Fig. 1, including maximum air and soil temperatures, average relative humidity, and total precipitation.

### 2.3. Sampling, sample preparation, and chemical analysis

Collected soil sediment samples, free from plant residues, were thoroughly mixed and sieved with a 2-mm screen. Water-soluble Se and B concentrations and salinity (EC) were determined in a soil water extract of 1:1 and processed as described by Bañuelos and Meek (1990), while total Se was determined after wet-acid digestion described by Bañuelos and Akohoue (1994). Selenium and B in soil samples were analyzed by an atomic absorption spectrophotometer (Thermo Jarrell Ash, Smith Hieftje 1000, Franklin, MA) with an automatic vapor accessory (AVA 880) and an inductively coupled plasma spectrometer (Perkin–Elmer Plasma 2000 Emission Spectrometer, Norwalk, CT), respectively. The National Institute of Standards and Technology (NIST) coal fly ash [Standard reference materials (SRM) 1633; Se content of 10.3 ± 0.6 mg $kg^{-1}$, with a recovery of 93%] was used as an external quality control standard for the soils. The general soil/sediment chemical properties of the research site at time of planting are summarized in Table 2. Plants were harvested or clipped from a minimum of nine 1-$m^2$ areas located near the soil sampling site for each crop. Wild-type *Brassica* plants were separated into stem and leaves. All plant materials were washed with deionized water, dried at 50 °C for 7 d, weighed, and ground in a stainless steel Wiley mill equipped with a 0.83 mm screen. Plant tissues were wet digested with $HNO_3$–$H_2O_2$–HCl as described by Bañuelos and Akohoue (1994). Selenium and B were analyzed as already described for soil samples. NIST wheat flour (SRM 1567, Se content of 1.1 ± 0.2 mg $kg^{-1}$, with a recovery of 94%) was used as an external quality control standard for plant Se.

### 2.4. Measurement of Se volatilization

During the active growing seasons for the perennial plants, measurements of volatile Se were taken four to eight times during each of the selected time periods (i.e., early, mid, and late growing seasons). The designated time periods were defined as follows: early growing season from May 1 through July 15; mid growing season from July 15 through October 1, and late growing season from October 1 through December 15. Measurements were not taken during dormancy of the perennial plants. Because the wild-type *Brassica* grew faster than the perennial species, volatile Se was collected more frequently in the *Brassica* field; 3–11 measurements were made during each month from May 2002 to February 2003. The chambers used for volatile Se collection were made of 6.6-mm thick Plexiglas and had dimensions of 0.71-m long, 0.71-m wide and 0.76-m high, as described in detail by Lin et al. (1999). Each chamber enclosed an area of 0.5 $m^2$ and had an internal volume of 0.38 $m^3$. Volatile Se was trapped in an alkaline peroxide trap solution (6% $H_2O_2$ and ~0.05 M NaOH). The solutions were contained in a series of three 500-ml gas-washing bottles (Corning 31760C), and each bottle contained 200 ml of the trap solution. The gas-washing bottles were connected to the outlet port of each chamber and to each other with Teflon tubing. The volatile Se produced inside each chamber was captured by pulling air out of the chamber through the trap solution with a 1/3-horse power vacuum pump.

Before field volatilization sampling was initiated, the efficiency of the chamber collection system was evaluated under controlled lab conditions. This was accomplished by sealing the bottom of the chamber to a sheet of Plexiglas with a gasket sealer. The recovery rate of volatile Se (as dimethyl selenide (DMSe), Alfa Aesar) was evaluated by spiking the chamber with different amounts of DMSe: 0.01, 0.1, 1.0, and 10.0 mg Se, respectively, while keeping the airflow and sampling duration (24 h) constant. The recovery rate ranged from 94% to 96% for each amount of DMSe. The effects of sampling duration and airflow rates on the recovery of volatile Se were also evaluated. The optimum sampling duration was found to be 24 h after evaluating the recovery rate of 0.1 mg Se as DMSe added to the collection chamber for 12, 24, and 48 h (data not shown). The most favorable airflow rate of 0.43 $m^3$ $h^{-1}$ was used

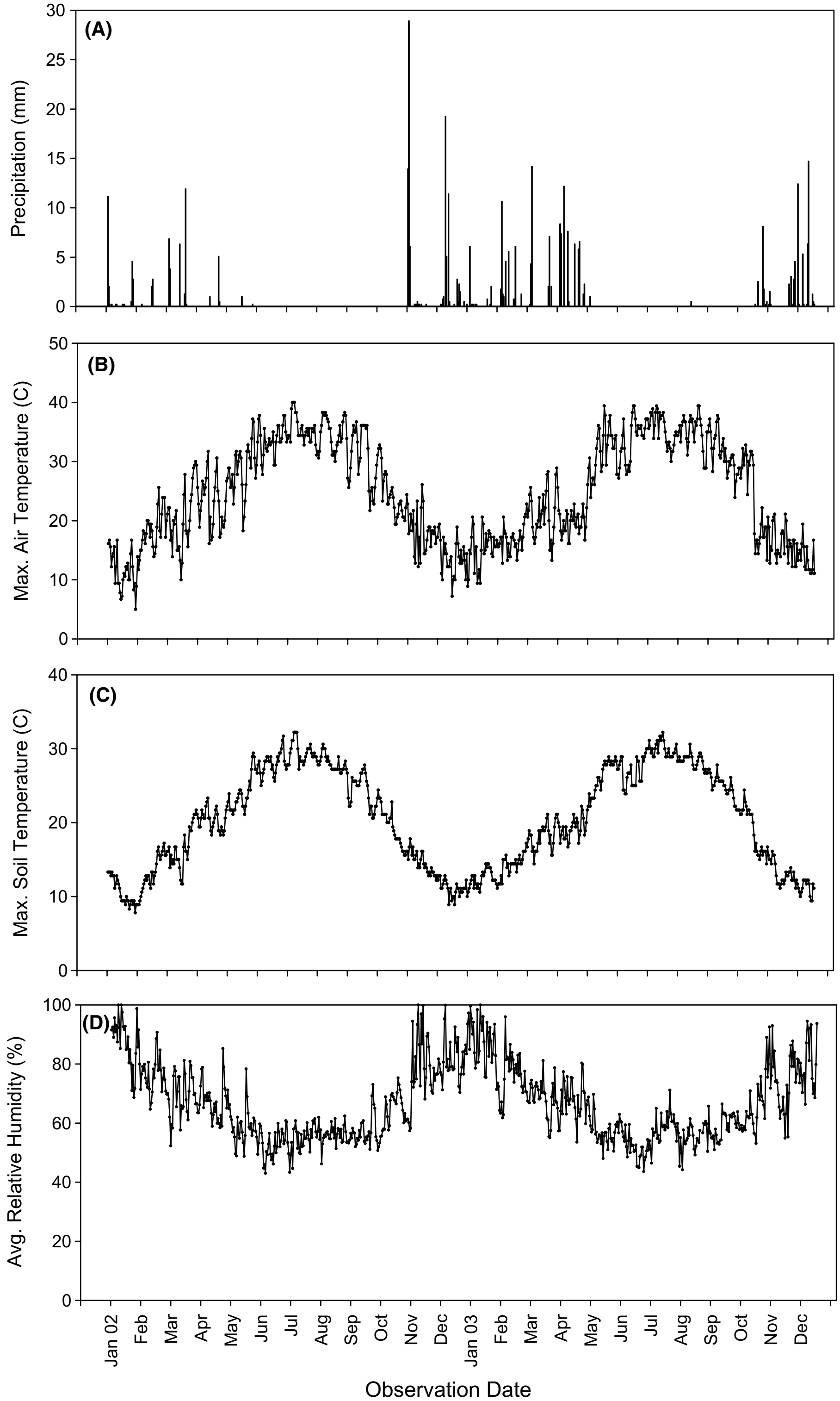


Fig. 1. Total precipitation (A), maximum air temperature (B), soil temperature (C), and average air relative humidity (D) for the field plots during the growing seasons of 2002–2003.

Table 2
Mean pre-plant soil levels of total Se and water extractable parameters between 0 and 45 cm for different treatment plots in drainage sediment

| Treatment plots | Total Se ($mg\ kg^{-1}$) | Water extractable ($mg\ kg^{-1}$) | | | EC ($mS\ cm^{-1}$) | pH |
|---|---|---|---|---|---|---|
| | | Se | S | B | | |
| Irrigated bare | 5.9 ± 2.4[a] | 0.2 ± 0.1 | 1584 ± 195 | 12.1 ± 0.3 | 17.3 ± 0.4 | 7.9 ± 0.1 |
| Non-irrigated bare | 4.4 ± 2.0 | 1.3 ± 1.1 | 2838 ± 765 | 14.0 ± 4.1 | 15.1 ± 4.7 | 8.2 ± 0.7 |
| Wild-type *Brassica* | 7.1 ± 3.9 | 0.6 ± 0.6 | 3799 ± 750 | 12.2 ± 1.7 | 9.8 ± 2.6 | 8.1 ± 0.2 |
| Elephant grass | 4.3 ± 1.3 | 0.2 ± 0.2 | 1178 ± 318 | 14.6 ± 0.9 | 9.0 ± 0.7 | 7.9 ± 0.1 |
| Saltgrass-turf/forage | 3.0 ± 1.2 | 0.2 ± 0.1 | 1866 ± 152 | 13.7 ± 1.6 | 12.9 ± 1.1 | 7.9 ± 0.1 |
| Leucaenia | 6.1 ± 2.5 | 1.1 ± 0.5 | 1814 ± 268 | 12.1 ± 0.7 | 13.1 ± 1.7 | 7.9 ± 0.1 |
| Salado alfalfa | 3.2 ± 1.4 | 0.2 ± 0.1 | 1531 ± 164 | 13.7 ± 1.8 | 12.6 ± 0.6 | 7.9 ± 0.1 |
| Salado grass | 4.4 ± 1.9 | 0.2 ± 0.1 | 1166 ± 388 | 13.2 ± 2.1 | 13.3 ± 1.1 | 8.0 ± 0.1 |
| Cordgrass | 8.2 ± 3.2 | 0.3 ± 0.2 | 1483 ± 439 | 9.6 ± 1.5 | 9.6 ± 1.3 | 8.0 ± 0.1 |

[a] Values presented represent the mean from different site locations ($n = 12$) and ± standard deviation.

after evaluating the recovery rate of 0.1 mg Se as DMSe at an airflow rate of 0.22, 0.43, and 0.86 $m^3\ h^{-1}$ (data not shown). The recovery of volatile Se showed that the percentage of total volatile Se recovered (with 0.1 mg Se as DMSe) in the three respective gas-wash bottles was 93%, 7%, and 0%, respectively (data not shown), indicating that there was no breakthrough of volatile Se from our sampling system.

Under field conditions sampling chambers were placed 5–10 cm into the soil, and packed with soil to prevent any losses of volatile Se. A freshly prepared alkaline peroxide trap solution was transferred into gas-washing bottles and the collection of volatile Se was initiated. To keep the alkaline peroxide stable in the trap solution at high summer temperatures in Central California, the gas-washing bottles were enclosed inside a Styrofoam chest containing ice packs adjacent to the chamber. Volatile Se was sampled for 24 h continuously, after which the solutions from three gas-washing bottles were collected and taken to the lab for Se analysis (Lin et al., 2002).

### 2.5. Statistical analysis

Statistical analysis was performed using the Statistical Analysis System (SAS) (SAS, 1988). Multiple comparisons among different seasonal means were conducted by PROC GLM with Tukey option.

## 3. Results

### 3.1. Plant growth

Among the plant species grown in drainage sediment, elephant grass and salado alfalfa produced the greatest and lowest amount of biomass, respectively (Table 3). Although all tested plant species established successfully in the drainage sediment plot, salado alfalfa, *Leucaenia* (*Leucaenia leucocephola*), elephant grass, and wild type-*Brassica* species were visually stunted in comparison with the same species in the control plot. Table 3 shows that salado grass, cordgrass, saltgrass-turf and -forage exhibited greater dry weight yields in the sediment plots compared to the same plant species planted in the sandy loam soil (control). Among all the plant species, elephant grass was the only species that showed apparent B toxicity (e.g., necrosis) on the leaf margins.

### 3.2. Bioaccumulation of Se, B, S, and Cl

Among the plant species, wild-type *Brassica* accumulated the highest concentrations of Se, S, and Cl. For example, the Se concentrations in *Brassica* were 48 mg Se $kg^{-1}$ DM compared to <10 mg Se $kg^{-1}$ DM in other plant species (Table 3), S concentrations were 2.5 g S $kg^{-1}$ DM compared to <0.7 g S $kg^{-1}$ DM in other plant species, and Cl concentrations were 4.1 g Cl $kg^{-1}$ DM in wild-type *Brassica* compared to 0.6 g Cl $kg^{-1}$ DM (the lowest) in elephant grass (Table 3). Boron concentrations were, however, the highest in elephant grass (≈920 mg $kg^{-1}$ at the first clipping), followed by *Leucaenia* and wild-type *Brassica* with 278 and 248 mg $kg^{-1}$ DM, respectively, and less than 100 mg B $kg^{-1}$ DM for other plant species (Table 2).

### 3.3. Rates of Se volatilization in the drainage sediment plots

Rates of Se volatilization from the vegetated plots were statistically higher than in the irrigated bare plots, while the rates in irrigated bare plots were higher than in the non-irrigated bare plots (Table 4; Fig. 2). Among the plant species, the mean daily rates (μg Se $m^{-2}\ d^{-1}$) of Se volatilization in the vegetated plots in 2002 were as follows: wild-type *Brassica* (39) > saltgrass-turf (31) > cordgrass (27) > saltgrass forage (24) > elephant grass (22) > salado grass (21) > *Leucaenia* (19) > salado

Table 3
Mean dry weight yield and concentrations of Se, S, B, and Cl in different crops grown in drainage sediment plots for 2002 and 2003 growing seasons; The control treatment was sandy loam soil (without drainage sediment)

| Plant species | Dry matter yields* ($g\ m^{-2}$) | | Concentration in plant ($mg\ kg^{-1}$ DM) | | | |
|---|---|---|---|---|---|---|
| | Control | Sediment | Se | S | B | Cl |
| Elephant grass ($n = 6$)** | 5967 (160)a | 3206 (81)***a | 7 (0.4)d | 1825 (57)f | 77 (2.2)†c | 6211 (139)f |
| Salado grass ($n = 6$) | 2105 (70)b | 2306 (80)c | 11 (0.7)bc | 3750 (84)c | 40 (1.5)d | 13420 (280)d |
| Cordgrass ($n = 6$) | 1221 (49)c | 1642 (59)d | 10 (0.7)bcd | 7120 (156)b | 35 (1.4)de | 33600 (685)b |
| Saltgrass-turf ($n = 4$) | 2209 (65)b | 2708 (72)b | 11 (0.6)bc | 3624 (80)c | 31 (1.3)e | 24920 (553)c |
| Leucaenia ($n = 4$) | 2575 (62)b | 2312 (69)c | 13 (0.8)b | 2675 (76)e | 278 (9.8)b | 7335 (150)ef |
| Salado alfalfa ($n = 8$)†† | 2502 (68)b | 1353 (43)d | 8 (0.5)cd | 2880 (78)de | 80 (3.1)c | 7200 (154)ef |
| Saltgrass-forage ($n = 4$) | 2602 (73)b | 2907 (79)ab | 9 (0.5)cd | 3153 (80)cd | 23 (1.0)f | 10110 (243)de |
| Wild-type *Brassica* ($n = 6$) | 2225 (61)b | 1800 (55)d | 48 (2.8)a | 24025 (546)a | 248 (9.6)a | 41502 (861)a |

* Mean annual total dry matter of plants grown in either control or sediment plots, which includes all clippings from perennial crops for all replications for 2002 and 2003 growing seasons. Means followed by the same letter are not significantly different at the $P < 0.05$ level within each column.
** Total number ($n$) of replications for each species.
*** Values represent the mean and standard error in parenthesis for two years.
† Mean B concentration at first clipping was 920 $mg\ kg^{-1}$, while 77 $mg\ kg^{-1}$ was the mean concentration from clippings two through four.
†† Data are presented for only one year due to crop destruction by gophers.

Table 4
Mean rates of Se volatilization from bare plots and different perennial cropped plots during the 2002 and 2003 growing seasons

| Treatment plots | 2002 ($\mu g\ m^{-2}\ d^{-1}$) | | | 2003 ($\mu g\ m^{-2}\ d^{-1}$) | | |
|---|---|---|---|---|---|---|
| | Early | Mid | Late | Early | Mid | Late |
| Non-irrigated bare | 3 (0.5)*d | 8 (0.5)g | 6 (0.6)g | 6 (0.4)e | 7 (0.5)e | 5 (0.4)d |
| Irrigated bare | 9 (0.7)c | 14 (0.9)f | 9 (0.6)fg | 14 (0.8)d | 17 (0.9)d | 11 (0.8)c |
| Elephant grass | 20 (0.9)a | 29 (1.0)d | 16 (0.8)d | 20 (0.9)c | NA** | NA** |
| Salado grass | 18 (0.9)a | 20 (0.8)e | 24 (1.1)b | 28 (1.2)b | 50 (1.8)a | 38 (1.9)a |
| Cordgrass | 17 (0.8)ab | 36 (2.1)c | 28 (1.2)a | 18 (0.8)c | 35 (1.7)b | 24 (1.1)b |
| Saltgrass-turf | 18 (0.8)a | 56 (2.0)a | 20 (0.7)c | 26 (1.0)b | NA*** | NA*** |
| Leucaenia | 14 (0.9)b | 30 (1.8)d | 12 (0.7)ef | 22 (1.1)c | 21 (1.2)c | NA** |
| Salado alfalfa | 15 (0.6)b | 15 (0.7)f | 13 (0.6)de | NA*** | NA*** | NA*** |
| Saltgrass forage | 10 (0.5)c | 42 (1.7)b | 20 (0.8)c | 53 (1.9)a | NA*** | NA*** |

* Values represent the mean followed by the standard error in parenthesis during early, mid, and late parts of the respective growing seasons. Means followed by the same letter are not significantly different at the $P < 0.05$ level within each column. Collection times were as follows: early (May 1–July 15), mid (July 15–October 1), and late (October 1–December 15).
** Plants were too large for volatilization chambers.
*** NA—not applicable because plant roots were destroyed by gophers.

alfalfa (14) > irrigated bare plot (11) > non-irrigated bare plot (6). Rates of Se volatilization in 2003 with limited field measurements were shown as follows: salado grass (39) > cordgrass (36) > irrigated bare plot (14, estimated from data in Table 4 and Fig. 2). Generally, the greatest amount of volatile Se was produced in summer months for all plant species during 2002 and 2003 growing seasons (Table 3, Fig. 2). The wild-type *Brassica* plot generated approximately 7-fold more volatile Se than the irrigated bare plot in summer months and approximately 2-fold more in the winter months. In particular, the wild-type *Brassica* plot produced the greatest amount of volatile Se during August (e.g., a mean of 73 μg Se $m^{-2}\ d^{-1}$ with a maximum rate of 120 μg Se $m^{-2}\ d^{-1}$). The rates of Se volatilization in the vegetated plots were significantly higher in 2003 than the rates observed in 2002 (Table 3). Among plots vegetated with the perennial plants, the salado grass plot consistently produced the highest amount of volatile Se (up to 50 μg Se $m^{-2}\ d^{-1}$) for both years (Table 3). Due to gophers and their periodic eating of the roots of salado alfalfa, saltgrass turf and forage, measurements of volatile Se were severely limited in those vegetated plots in late 2003. In addition, because the heights of the elephant grass and *Leucaenia* had exceeded the physical dimensions of the collection chamber in 2003, measurements

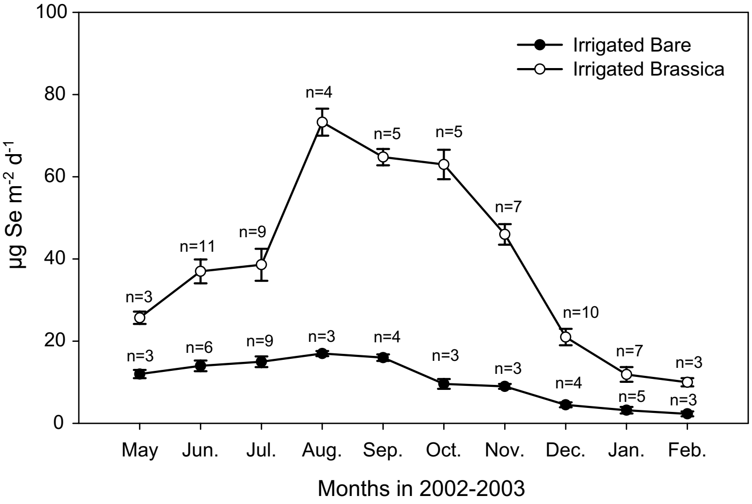


Fig. 2. Mean monthly rates of Se volatilization from irrigated-bare and wild-type *Brassica* plots during 2002–2003. Values are the means from the respective *n* values with standard errors. All values between irrigated-bare and irrigated-*Brassica* were significantly different ($P < 0.05$) from one another for each tested month. Irrigated bare plots received the same rate of water application as the wild-type *Brassica* plots.

of volatile Se in those plots were terminated after mid 2003 (see NA in Table 4).

### *3.4. Se removal by phytoextraction compared with biological volatilization*

An estimated comparison between plant accumulation and biological volatilization of Se indicates that wild-type *Brassica* and *Leucaenia* were the most effective in removing soluble Se from the soil surface in 10 months and two years respectively. For illustrative purposes, a general mass balance on soluble Se available in sediment at preplant and amount of lost Se occurring with the plant-based technology was estimated for a depth of 0–15 cm (i.e., the major root zone in the sediment field). We calculated that 149 mg of soluble Se would be available from 0 to 15 cm in a 1 $m^2$ area with a total soil dry weight of 149 $kg^{-1}$ $m^{-2}$ at a selected concentration of 1 mg Se $kg^{-1}$ (values ranged from 0.2 to 1.3 mg $kg^{-1}$ at 0–45 cm). By estimating the amount of Se mass accumulated in above-ground plant material (e.g., Se mass = yield × shoot Se concentration), wild-type *Brassica* accumulated 87 mg of Se for a 10 month growing season. With the mean rate of Se volatilization (see Fig. 2) for the wild-type *Brassica* plot, an additional 11 mg of Se (e.g., approximately, the mean volatilization rate for each respective month (total of 10 months) × 30 days) was removed via volatilization. Hence, the wild-type *Brassica* removed up to 66% or 98 mg of the estimated available Se as soluble Se from the upper 15-cm depth (i.e., the zone of most active root and microbial activity) in 10 months. Table 5 shows the approximated Se removal efficiency (%) for the perennial plant species that were calculated similarly (vs. 10 month growing season for the wild-type *Brassica*) for their respective growing periods of two years. Estimated Se removal percentages show that the vegetated plots removed between 20% and 70% of the estimated soluble Se from the 0–15 cm layer of the drainage sediment compared to less than 5% in either the irrigated bare or non-irrigated bare plots, respectively (Table 5). It appears, based on this preliminary observation (data in Tables 3 and 5), that plant accumulation of Se is more effective than biological volatilization for removing soluble Se from the drainage sediment at a given concentration of 1 mg $kg^{-1}$. Plant accumulation of Se and its contribution to Se removal at different depths in sediment at post-harvest is presently being evaluated and will be discussed in great detail in another paper.

## 4. Discussion

### *4.1. Factors affecting Se volatilization in drainage sediment*

Field measurements taken for two years showed that Se volatilization from drainage sediment occurred in vegetated and irrigated bare plots, and to a lesser extent in non-irrigated bare plots. Rates of Se volatilization from the vegetated plots were always greater than bare plots (Table 5). Because the Se-collection chambers presumably collected volatile Se produced by both plants and microbes, it was not the intent of this study to quan-

Table 5
Estimated amounts of Se as soluble Se from 0 to 15 cm depth removed via plant accumulation and volatilization in treatment plots

| Treatment plots[a] | Se removed via[b] ($mg\ m^{-2}$) | | Se removal efficiency[c] (%) |
|---|---|---|---|
| | Accumulation | Volatilization | |
| Elephant grass | 45 | 12 | 38 |
| Salado grass | 51 | 16 | 45 |
| Cordgrass | 33 | 14 | 32 |
| Saltgrass | 60 | 18 | 52 |
| Leucaenia | 60 | 10 | 70 |
| Salado alfalfa | 22 | 8 | 20 |
| Salado forage | 52 | 13 | 44 |
| Wild-type *Brassica* | 87 | 11[e] | 66 |
| Irrigated bare | NA[d] | 7 | 5 |
| Non-irrigated bare | NA | 3 | 2 |

[a] All crops, except wild-type *Brassica*, had a nine month growing season and three month dormancy for 2002 and 2003 respectively.
[b] Calculations for all crops, except *Brassica*, were based upon data from two 9 month growing seasons (early, mid, late) presented in Tables 2 and 3. Accumulated Se removed is based upon total yield for 2002 and 2003 × plant Se concentration (Table 2) and volatilized Se removed is based upon early, mid, late volatile Se values (Table 3) × 90 days, respectively. The same volatile Se values from growing season 2002 were used for calculation of NA values in Table 3 for the respective plant species in 2003.
[c] Based upon an extractable soil concentration of 1 $mg\ kg^{-1}$ and a total soil dry weight of 149 $kg^{-1}\ m^{-2}$ 15 cm depth, 149 mg of Se were available per $m^2$. The Se removal efficiency percentage was estimated by dividing the calculated Se removed via accumulation and volatilization by 149 mg of extractable Se.
[d] NA—not applicable, because no plants were present in bare plots.
[e] Estimations for *Brassica* were derived by using monthly rates of Se volatilization (Fig. 2) × 30 days × 10 months (one growing season).

tify the amounts of volatile Se contributed respectively by plant and soil microbes, and/or both. The measurement of volatile Se from irrigated bare plots implies, however, that soil microbial and fungal induced volatilization also occurred in the field (Cahn et al., 1976; Frankenberger and Karlson, 1989a,b).

Among the tested plant species, the plots with annual wild-type *Brassica* volatilized the greatest amount of Se on a mean daily basis within 10 months. Different *Brassica* species have been reported by others to be efficient volatilizers of Se under less adverse conditions than those in this field study (Zayed and Terry, 1994; Zayed et al., 1998). Despite the lower rates of Se volatilization measured from the plots with perennial grasses, e.g., saltgrass, cordgrass, their low maintenance characteristic and their ability to grow well year after year in the sediment plots should be acknowledged. For all plant species the estimated removal of soluble Se via volatilization was always lower than that Se removed via phytoextraction. It is uncertain whether volatilization rates would increase as perennial plants produced more biomass below and above ground over time.

The highest rates of Se volatilization for all treatment plots were observed during the summer months (e.g. mid collection). The higher soil temperatures and increased biological activity during this hot season likely attributed to the higher production of volatile Se (Lin and Terry, 2003). The rates of Se volatilization observed in this study were generally comparable to rates that were reported under similar environmental conditions (Hansen et al., 1998; Terry and Lin, 1999; Lin et al., 2000). For example, Lin et al. (2002) observed in a 12-month field study that saltgrass (*Distichlis spicata* L.) volatilized an average rate of 11 ± 8 $\mu g\ Se\ m^{-2}\ d^{-1}$, which is comparable to an average of 25 ± 12 $mg\ Se\ m^{-2}\ d^{-1}$ for saltgrass in this drainage sediment study. Under marsh conditions others have also measured volatile Se as high as 190 and 175 $\mu g\ Se\ m^{-2}\ d^{-1}$ for *Polypogon* sp. (Hansen et al., 1998) and *Bromus* sp. (Zawislanski and Zavarin, 1996), respectively. The differences between the reported rates of volatile Se and the presently observed rates were likely resulted from many factors, including (1) the forms of Se species present in the sediment–soil (e.g., reduced or oxidized forms), (2) the high salinity and soluble B content in the sediment/soil, (3) the high levels of sulfate in the sediment/soil (up to 3800 $mg\ kg^{-1}$) and in the plant tissue (up to 2.4%), and (4) the absence of organic matter (<0.1% from 0 to 45 cm depth). All plant materials were removed throughout the growing seasons to prevent introducing Se back into the sediment plots as Se-enriched plant material. Organic matter has, however, been reported to be critically important for promoting microbial volatilization of Se (Frankenberger and Karlson, 1989a,b). High levels of soil salinity may result from sulfate salinity (e.g., $Na_2SO_4$) or chloride salinity (e.g., NaCl). In the western part of the SJV or in the drainage sediment in the Saint Luis Drain, high soil salinity was mainly due to high levels of sulfate. Because sulfate and selenate are chemical analog, sulfate competes with selenate for uptake by the sulfate transporter as well as for the enzymes of the Se assimilation and volatilization pathway in plant tissues. Therefore, selenate uptake and volatilization by most plant species can be significantly inhibited by the increase of sulfate in soil (Zayed and Terry, 1994). On the contrary, chloride salinity had much less effect on selenate uptake and volatilization than sulfate salinity (Terry et al., 2000).

Preliminary speciation of Se in drainage sediment plots showed that the average concentration of soluble selenate and selenite were $2.3 \pm 2.0$ and $1.5 \pm 0.5$ mg kg$^{-1}$, respectively, and the average concentrations of elemental and organic Se were $5.6 \pm 1.5$ and $4.4 \pm 3.8$ mg kg$^{-1}$, respectively (Banuelos et al., unpublished data). It is more difficult energetically to volatilize selenate than selenite or other organic forms of Se by microbes and plants (Frankenberger and Karlson, 1994; Terry et al., 2000). Additionally, Frankenberger and Karlson (1989a,b) and Losi and Frankenberger (1997) found that Se volatilization rates by soil microbes were higher from organic Se or $SeO_3^{2-}$ as the Se source when compared with $SeO_4^{2-}$. The forms of Se present in soils also influenced rates of Se volatilization by plants (Zayed et al., 1998). Several researchers have pointed out that Se volatilization by plants proceed more rapidly if Se is available in more reduced forms (e.g., selenite or selenomethionine) as compared to selenate (Zayed et al., 2000). Zhang and Moore (1997) indicated that the concentration of dissolved organic Se is a more important factor affecting Se volatilization from plants and sediments than dissolved inorganic Se.

### *4.2. Fate of biogenic volatile Se in the environment*

Biological volatilization of Se represents an environmentally friendly and potentially effective biotechnology for the remediation of Se-contaminated water and soil in the SJV. The predominant chemical form of volatile Se, DMSe, can be rapidly diluted in the air, oxidized, and converted into aerosol- and particulate-associated Se in the atmosphere. Atkinson et al. (1990) reported that DMSe can react with OH, $NO_3$ radicals, and $O_3$ in a few hours or less in the lower troposphere. The unknown Se products could be absorbed onto airborne submicron-sized particulates and travel considerable distances in the atmosphere and be deposited downwind (Gao and Tanji, 1995). Lin et al. (2000) further reported on the probable long-range transport and likely destinations of volatile Se produced in the SJV. Their results from the air mass forward trajectory analysis suggested that due to strongly unstable thermal stratification conditions in the SJV, the biogenic volatile Se from contaminated sites in the western San Joaquin Valley is likely to be transported out of the Valley within the first 24 h toward other mountain areas where Se contamination is not a concern. Overall, given the amount and fate of Se produced via biological volatilization, Se input to the atmosphere would not likely induce detrimental effects on local humans and wildlife ($CH_2M$ Hill, 1988).

## 5. Conclusions

The biological process of Se volatilization in drainage sediment needs to be enhanced substantially under field conditions. Although plots with wild-type *Brassica* plants volatilized more Se than with the other perennial plants, the maintenance of the perennial plants was considerably low. Because they can be repeatedly clipped, a large amount of Se-enriched plant material produced may be potentially of importance to animal producers who may use the harvested product as a source of Se supplement for sustaining the health of their animals. Work in progress shows that the addition of organic amendments and genetically engineered *Brassica* plants contribute to a greater volatilization of Se in the same sediment plots. Further evaluation may show that plant accumulation of Se (e.g., phytoextraction) with current genotypes and management approaches may be an effective approach for removing Se from drainage sediment.

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